

Water Quality Improvement through Bioretention Media: Nitrogen and Phosphorus Removal

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ABSTRACT: High nutrient inputs and eutrophication continue to be one of the highest priority water quality problems. Bioretention is a low-impact development technology that has been advocated for use in urban and other developed areas. This work provides an in-depth analysis on removal of nutrients from a synthetic stormwater runoff by bioretention. Results have indicated good removal of phosphorus (70 to 85%) and total Kjeldahl nitrogen (55 to 65%). Nitrate reduction was poor (<20%) and, in several cases, nitrate production was noted. Variations in flowrate (intensity) and duration had a moderate affect on nutrient removal. Mass balances demonstrate the importance of water attenuation in the facility in reducing mass nutrient loads. Captured nitrogen can be converted to nitrate between storm events and subsequently washed from the system. Analysis on the fate of nutrients in bioretention suggests that accumulation of phosphorus and nitrogen may be controlled by carefully managing growing and harvesting of vegetation. *Water Environ. Res.*, **78**, 284 (2006).

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Introduction

Eutrophication continues to be one of the top quality concerns in many water bodies. Nitrogen and phosphorus, the primary nutrients implicated in eutrophication, enter water bodies via a variety of pathways. For example, the three major sources of nutrients to the Chesapeake Bay (CBP, 2004) are agricultural runoff (approximately 40%), point sources (approximately 20%), and urban and septic discharges (approximately 15%). Considerable emphasis has been placed on the development of technologies and practices to mitigate nutrient input from the first two sources. Because of this, in conjunction with continued population growth and urbanization, the third source represents an increasingly important input (CBP, 2004). Urban runoff quality improvement, because of limited and costly land area, combined with flood control concerns, represents a unique challenge in this regard.

In response to these challenges, the philosophy of low-impact development (LID) is developing increasing interest. With LID, land is developed such that the resulting hydrologic and water quality characteristics remain as close as possible to those of the undeveloped land (Holman-Dodds et al., 2003; Rushton, 2001). Impervious area is reduced and flow is shifted to small, distributed infiltration technologies throughout the developed area. Bioretention is a mulch/soil/plant-based stormwater best management practice (BMP) that is an integral part of the LID philosophy. Stormwater is directed to a bioretention area, where it pools (typically 15 to 30 cm) and infiltrates. Between precipitation events, however, the bioretention cell is designed to remain dry. The primary treatment

medium is a sandy soil, typically 75 to 120 cm deep. A 5- to 8-cm shredded hardwood mulch layer is added on the surface to maintain soil moisture and filter incoming sediment. Native plant species are planted in a random layout to imitate an upland terrestrial ecosystem. A plastic perforated pipe underdrain is typically placed below the media layers. Water quality improvement in bioretention occurs through evapotranspiration, soil filtering, adsorption, biotransformation, and other natural mechanisms. The infiltration processes smear peak flows, and groundwater recharge is emphasized.

Recently, laboratory- and pilot-scale bioretention box studies were completed to provide proof-of-concept for pollutant removal in bioretention (Davis et al., 2001). Measured removals of heavy metals were generally >95%. Good removal of total phosphorus (approximately 80% from an input concentration of 0.5 mg/L as phosphorus [P]), total Kjeldahl nitrogen (TKN) (50 to 75% from an input of approximately 3.5 mg/L), and ammonium (60 to 80%, 1.2 to 2.4 mg/L as nitrogen [N] input) were also found, though nitrate removal was poor. Overall, these studies supported bioretention as an efficient treatment practice. Subsequent detailed work on the capture and fate of heavy metals in pilot-scale bioretention studies has demonstrated that copper, lead, and zinc tend to accumulate in the surface layers of the bioretention media and variations in runoff event intensity (2.6 to 8.2 cm/h) and duration (3 to 12 h), pH (6 to 8), and metal concentrations (30 to 120 µg/L for copper [Cu] and lead [Pb], and 300 to 1300 µg/L for Zn) had minimal effect on bioretention metal removal performance (Davis et al., 2003). Bypass of the bioretention treatment at high flow or long duration was the only event that resulted in significant metal passage beyond the bioretention barrier. Long-term metal buildup was evaluated and becomes a concern for bioretention operation beyond 15 years.

Limited data on stormwater infiltration practices show them to be moderately effective in nutrient removals. Median or average removal efficiencies reported were 65% for total phosphorus, 83% for both ammonia-nitrogen and total N, and 82% for nitrate (U.S. EPA, 1999). Updated information from the Center for Watershed Protection (CWP, 2004) lists median removals of total phosphorus and total nitrogen at 70 and 51%, respectively. Hunt et al. (2002) noted total nitrogen removals exceeding 80% for laboratory bioretention columns. Preliminary results also indicated significant total nitrogen (TN) reduction in North Carolina field facilities. Detailed performance analysis of Austin sand filters (Barrett, 2003) has noted reduction of TKN, but export of nitrate, with TN reduction of 22%, and 39% total phosphorus (TP) reduction.

In studies on related stormwater management practices, a compilation of data for wetlands to treat runoff shows nitrate removals

Table 1.—Target chemical makeup of water applied as synthetic runoff to bioretention systems.

Pollutant	Chemical	Concentration (mg/L except for pH)
Nutrients		
Nitrate	NaNO ₃	0.4 (as N)
Organic N	Glycine	4 (as N)
Phosphorus	Na ₂ HPO ₄	0.5 (as P)
Dissolved Solids	CaCl ₂	120
pH	HCl/NaOH	7.0
Heavy Metals		
Copper	CuSO ₄	0.08
Lead	PbCl ₂	0.08
Zinc	ZnCl ₂	0.6

from –193% (nitrate export) to 99% (Carleton et al., 2001). The TP data were only slightly less variable, ranging from –55% to 89%. Rushton (2001) noted that vegetated swales improved runoff water quality from a commercial parking lot. Nitrogen, total suspended solids (TSS), and metal loads were reduced through reduction in concentrations combined with water infiltration. Some export of phosphorus was noted, however. Yu et al. (2001) found grass swales to be effective in reducing TSS, chemical oxygen demand (COD), TN, and TP concentrations in runoff flows. In both of these studies, runoff infiltration was found to be important in reducing pollutant loadings, and, for small storm events, the entire flow volume was infiltrated, resulting in zero pollutant discharge from the treatment practice.

Fertilizers and decay of vegetation, along with atmospheric deposition, are primary sources of nutrients in urban areas. Measured values of nutrients in urban and roadway runoff report TKN concentrations of 0.2 to 18 mg/L, with a typical value of 1.2 mg/L, and oxidized nitrogen (NO₃ + NO₂-N) from 0.0 to 2.3 mg/L, with 0.5 mg/L as representative (all as N). Total and ortho- P measurements ranged from 0.02 to 9.4 mg-P/L, with a typical value of approximately 0.4 mg/L (Ackerman and Schiff, 2003; Barrett et al., 1998; Brezonik and Stadelmann, 2002; Cordery, 1977; Wu et al., 1996 and 1998). Significant nutrient loads can also be added to LID practices through construction, maintenance, and management operations that may include addition of soil or mulch media that are high in nutrients or fertilization processes used to establish new or injured vegetation.

Biologically mediated pathways, involving both microorganisms and the vegetation in the bioretention facility, should be important in controlling nutrient fate in bioretention. These biological processes may be too slow to provide a significant effect to runoff nutrient levels during actual runoff events, but may induce major alterations to nitrogen balances during the time between rainfall events. Microbial conversion of nitrogen species to various forms (ammonia, nitrate, N₂) will alter nitrogen capture, mobility, and buildup.

The objective of this work was to provide a relatively comprehensive investigation of nitrogen and phosphorus removal and fate in bioretention media, based on current bioretention design, as was previously done with heavy metals (Davis et al., 2003). Parameters studied include runoff event duration and intensity, pH, and nutrient concentrations. Results from two controlled field studies are used

to support this work. With the growing importance of nutrients in many water quality issues, especially in urbanized areas, bioretention represents an important technological tool that holds promise to address these problems. Long-term nutrient accumulation and mass balance issues are discussed, as they have ramifications on system design life and maintenance requirements.

Methodology

Bioretention Box Experiments. Experimental procedures for bioretention box studies have been described previously (Davis et al., 2001 and 2003). Briefly, a small bioretention test box (107 cm long by 76 cm wide, with a depth to hold 61 cm of media, plus a 15-cm freeboard) and a large box (305 cm long by 152 cm wide with a depth to hold 91 cm of media, plus a 15-cm freeboard) were constructed. Perforated polyvinyl chloride (PVC) pipes were installed at two depths (18 and 61 cm) in the small box and three depths (25, 56, and 91 cm) in the large box for collection of samples for water quality analysis. Each box was filled with a sandy loam soil (approximately 76% sand) and was topped with a 2.5-cm layer of mulch. Six small *Creeping juniper* plants with branches 13 to 18 cm long were installed in the small box; 12 small and 12 large *Creeping juniper* plants were established in the large box. The boxes were designed to match bioretention design specifications typical of when they were constructed, as described in the Introduction. These boxes were used to provide pollutant removal information for bioretention under controlled laboratory conditions. While the larger box had dimensions more similar to a field bioretention facility, the smaller box was more flexible for experimental variation and required much less input water and sample analyses, allowing collection of more data.

Synthetic runoff with characteristics as presented in Table 1 was prepared using dechlorinated tap water. Only the nitrogen and phosphorus results are presented in this study; metals results are discussed in Davis et al. (2003). Synthetic runoff was applied to the boxes at a standard rate of 4.1 cm/h for 6 hours, except as described below. Infiltrated water samples were collected from the lateral ports and from the input over the duration of the experiment. The bottom ports were always open; the upper ports were opened only for sampling. The flow duration or rate or the chemical makeup was varied from that described above to investigate effects of different operational conditions; in all cases, only one condition was varied at a time. Two or three repetitions were completed on the boxes for each condition, and all data were combined to obtain mean influent concentrations, mean effluent concentrations, and concentration reductions for the bioretention treatments. From 2 to 4 samples are used for the large box data and from 4 to 12 for the small box. Flowrates were measured, and infiltrated volumes were estimated for use in pollutant mass balance calculations.

Field Experiments. The field experiments were described in detail in Davis et al. (2003). Briefly, the runoff loading in both studies was also fixed at 4.1 cm/h for a 6-h duration over an area of approximately 5.3 m². The target water quality was that of Table 1. The first field study was at a facility that was constructed in 1992 at a shopping mall parking lot in Greenbelt, Maryland. These bioretention cells contained a sandy loam topsoil covered with approximately 5 cm of mulch and held a thick growth of grasses (90 to 120 cm tall) mixed with a few shrubs and small trees. An overflow drain in the facility allows a maximum of approximately 20 cm of water head during a rainfall event. A 15-cm diameter perforated PVC pipe was located at a depth of 114 cm to collect

infiltrated runoff. Grab samples were collected every 25 to 30 minutes in 125- or 1000-mL bottles, with random input samples.

The second experiment was completed June 1999 in Largo, Maryland. This facility was installed in 1998, with the media consisting of a mixture of 50% construction sand, 20 to 30% leaf mulch, and 20 to 30% topsoil. A 15-cm T-shaped underdrain runs the span of the entire system, branching to the inlet at an 83-cm depth. Bare mulch made up most of the surface, with some grasses, bushes, and small trees. A curb cut bypass allows approximately 15 cm of water ponding. Effluent water did not originate from the underdrain, but pooled near a crack in the floor of the storm drain invert at a depth of 128 cm. Grab samples were collected from this pool every 30 minutes. In both field studies, all samples were collected in acid-washed plastic bottles and transported to the Environmental Engineering Laboratory, University of Maryland (College Park, Maryland).

Analytical Methodology. The collected samples were analyzed for nitrate, phosphorus, and TKN, as described previously (Davis et al., 2001). Nitrate analyses were performed using a Dionex DX-100 ion chromatograph (Dionex, Sunnyvale, California). The TKN and TP were analyzed by *Standard Methods* 420A (APHA et al., 1985) or 4500-N_{org}B (macro-Kjeldahl method; APHA et al., 1995) and 424 (phosphorus; APHA et al., 1985) or 4500-P D (APHA et al., 1995). Although nitrite was not measured, as a first approximation of total N, values of TKN + NO₃-N are also tabulated and discussed. Statistical significance in comparing various runoff effects was evaluated using the students' t-test and a 95% confidence level with the null hypothesis that these runoff effects did not affect nutrient removal.

Results and Discussion

Bioretention Box Studies. Box laboratory studies were completed to examine bioretention performance over a range of different runoff behaviors and chemical characteristics. These conditions were varied individually, and the extent of their influence on the overall performance of bioretention was assessed and compared to the results obtained from "standard conditions" (4.1 cm/h for 6 h, Table 1 concentrations), which are described in Davis et al. (2001). Generally, nutrient concentrations varied little over the duration of a single experiment; exceptions are noted below. Mean values \pm 1 standard deviation are presented for both nutrient concentrations and percent removals. Compared to the metals results (Davis et al., 2003), the nutrients are removed to a much lesser extent and data show significantly more variability.

Duration and Flowrate (Intensity) Effects. Duration and intensity experiments were investigated to examine flow effects on the pollutant removal. Both will affect the pooling head and, therefore, the flow through the media. Faster flows may compromise pollutant uptake by limiting contact time. First, studies were completed for a three-hour duration, one-half that for the standard condition, followed by experiments at one-half the flow intensity (2 cm/h). The water head increased to a maximum of 5 to 9 cm in the small box over the 3-h duration and up to 3.5 cm for the low intensity, as compared to 6 to 12 cm for the 6-h standard duration. Results for the nutrient measurements and, for comparison, those from the standard condition studies are presented in Table 2. Because of experimental difficulties, nitrate data were not available from the standard study in the small box.

The TP removals from the lower duration and intensity studies increased with depth, up to 77 to 87% at the bottom of the boxes,

with the phosphorus discharge concentration reduced to 0.06 to 0.1 mg/L. Significantly less removal was noted for the upper sample ports. These results generally agree with values from the standard conditions results for both boxes, and the data did not provide evidence to reject the null hypothesis. Mean effluent concentrations for the small box studies were not statistically different from standard conditions. This effect is at least partially a result of the large variability in the removal rates for the standard conditions, which precludes precise estimation of the mean concentrations under standard conditions. The maximum head in the large box was 7.0 cm, as compared to 18 cm at the standard condition flowrate. Statistically, values for the large box were significantly different (upper and lower were less, but middle was greater), but the overall trend of greater TP removal with depth holds here.

Removals of 74 to 83% were noted for TKN. In contrast to phosphorus, a significant removal of TKN occurred by the time the flow reached the upper sample ports (42 to 63%), suggesting that the surface mulch layer plays an important role in TKN capture. Effluent TKN averaged 0.66 to 1.0 mg/L. These values and trends also do not differ from those of the standard conditions.

For both the low-duration and low-intensity studies, nitrate concentrations were observed to be higher than input in the small boxes. Nitrate export has been noted in our earlier bioretention box studies (Davis et al., 2001) and from sand filters treating urban runoff (Barrett, 2003). The output was 20 to 26% greater from the upper ports and 13 to 25% greater from the lower ports. In contrast, removals from 19 to 79% at the lowest port were found for the low intensity application in the large box. These are in contrast to nitrate production at the upper ports, followed by low nitrate removal (24%) at the lower ports, found from the standard conditions study. Although the differences in the mean values are relatively large, the variability found in the standard study prevents these differences from being statistically significant. The TKN + NO₃-N results are dominated by TKN because the input was nearly an order of magnitude greater. Total removals of 66 to 83% N were measured. Although the nitrate data suggest that nitrification is taking place in the bioretention boxes, the TN results suggest a net accumulation of nitrogen by the media.

Nutrient mass balances were evaluated by calculating the total species mass (M) input and output to the boxes as follows:

$$M = \int_0^{t_0} QC dt \quad (1)$$

Where

C = nutrient concentration, and

Q = water flowrate.

The integral is taken over the entire flow duration, t_D . For the input flow, with a constant Q and C , the input mass, M_I , is given by the following:

$$M_I = Q_I C_I t_D \quad (2)$$

The effluent mass (M_O) is given by the following:

$$M_O = \sum_{i=1}^n \sum_{t=0}^{t_E} Q_{(i,t)} C_{(i,t)} \Delta t \quad (3)$$

Where the products of the concentration, flow, and time increment are summed over the total time of effluent flow, t_E ; these values are summed over each bottom outlet in the box, n .

Table 2.—Summary table for nutrient removal for boxes at low durations and flow rates.

	Standard flow rate & duration, 6-hr, 4.1 cm/hr (Davis et al. 2001)				3-hour duration				Flowrate halved (2 cm/hr)			
	P (mg/L)	TKN (mg/L)	NO ₃ -N (mg/L)	TN ^a (mg/L)	P (mg/L)	TKN (mg/L)	NO ₃ -N ^c (mg/L)	TN ^{ac} (mg/L)	P (mg/L)	TKN (mg/L)	NO ₃ -N (mg/L)	TN ^a (mg/L)
Small Box												
Input	0.44 ± 0.04	3.5 ± 0.21	—	—	0.44 ± 0.01	3.5 ± 0.44	0.32 ± 0.01	3.8 ± 0.43	0.44 ± 0.03	3.9 ± 0.23	0.39 ± 0.01	4.2 ± 0.23
Average ± Std. Dev.												
U	0.37 ± 0.07	1.6 ± 0.98	—	—	0.40 ± 0.19	1.4 ± 0.78	0.39 ± 0.08	1.8 ± 0.70	0.35 ± 0.10	1.4 ± 0.82	0.49 ± 0.15	1.9 ± 0.85
L	0.13 ± 0.13	0.84 ± 0.29	—	—	0.10 ± 0.04	0.88 ± 0.46	0.40 ± 0.07	1.3 ± 0.44	0.07 ± 0.02	0.66 ± 0.45	0.46 ± 0.14	1.1 ± 0.55 ^d
Removal %												
U	15 ± 16	55 ± 28	—	—	7 ± 46	58 ± 23	(-20) ± 24	52 ± 19	21 ± 17	63 ± 20	(-26) ± 40	55 ± 19
L	71 ± 31	76 ± 8	—	—	77 ± 9	74 ± 13	(-25) ± 20	66 ± 11	83 ± 4	83 ± 12	(-13) ± 49	74 ± 13
Mass Removal (%)	82 ± 10	86 ± 4	—	—	87 ± 8	85 ± 10	35 ± 29	80 ± 10	87 ± 3	87 ± 3	13 ± 27	80 ± 7
Large Box												
Input	0.52 ± 0.04	2.8 ± 1.2	0.34 ± 0.00	3.1 ± 1.2	—	—	—	—	0.47 ± 0.02	3.7 ± 0.36	0.35 ± 0.01	4.1 ± 0.35
Average ± Std. Dev.												
U	0.52 ± 0.05 ^b	1.7 ± 0.51	0.67 ± 0.49	2.4 ± 0.92	—	—	—	—	0.42 ± 0.02 ^d	2.2 ± 0.52	0.28 ± 0.01	2.5 ± 0.51
M	0.14 ± 0.04	1.1 ± 0.57	1.0 ± 0.76	2.1 ± 0.74	—	—	—	—	0.21 ± 0.01 ^d	1.2 ± 0.33	0.31 ± 0.06	1.5 ± 0.31
L	0.10 ± 0.02	0.90 ± 0.74	0.26 ± 0.35	1.2 ± 1.0	—	—	—	—	0.06 ± 0.03 ^d	1.0 ± 0.38	0.07 ± 0.01	1.1 ± 0.37
Removal %												
U	1 ± 8 ^b	38 ± 15	(-96) ± 117	13 ± 38	—	—	—	—	11 ± 2	42 ± 14	19 ± 3	40 ± 13
M	73 ± 6	61 ± 17	(-205) ± 181	29 ± 12	—	—	—	—	54 ± 1	67 ± 11	11 ± 18	63 ± 10
L	81 ± 4	68 ± 27	24 ± 102	60 ± 31	—	—	—	—	87 ± 7	83 ± 13	79 ± 1	83 ± 12
Mass Removal (%)	99 ± 0	97 ± 2	97 ± 3	98 ± 1	—	—	—	—	99 ± 0	99 ± 0	99 ± 0	99 ± 0

(U=Upper Ports; M=Middle Ports; L=Lower Ports).

^a TN defined as TKN + NO₃-N.^b One point sequestered. Without this point, values are 1.5 ± 1.7 mg/L and (-179) ± 262%.^c Nitrate and TN values used as standard for comparison to other conditions since nitrate data were not available under standard conditions.^d t-test indicates significantly different from standard conditions at 95% confidence level.

Because only a fraction of the water passed through the boxes, the mass-based pollutant removals were always greater than the concentration-based removals. Under standard conditions, TP and TKN mass removals were 82 and 86%, respectively, in the small box. Even greater effect was demonstrated in the large box, with 97% or greater mass removal for all pollutants. A larger volume of the input water was held by the soil in the large box, eventually being lost through evapotranspiration. Even better results were noted in mass removals for the lower duration and flowrate because, with a smaller volume of water being added to the systems, a greater fraction of the total is held by the media. The most striking observation is that a positive mass removal of nitrate is noted, even though effluent concentrations were higher than input. Thus, attenuating the infiltrating runoff volume provides for significant enhancement of pollutant mass removal.

The next studies were carried out to simulate the conditions where the duration of the storm was doubled (12 h) or where the flowrate was doubled to 8.1 cm/h. The head increased to 15.5 cm in one small box experiment in the 12-h duration studies and for all high-flow-rate experiments (small and large boxes). This occurred at a duration of 2.25 to 7.5 h into the test, whereby the flowrate to the test box was decreased to maintain the head at approximately this level, specifically from 4.1 to 2.7 cm/h for the remaining treatment times. The other two experiments in the 12-h duration study resulted in head buildup just under the 15.5-cm

limit. The resulting higher head caused an increase in the infiltration rate through the boxes. This process mimics a field condition in which a system overflow bypass is installed at a height of 15.5 cm, with any water buildup above this value bypassing the bioretention treatment.

Limited removal was found with phosphorus from the upper ports (Table 3), and concentrations were observed to somewhat decrease with time for the long duration. Nonetheless, very good P removal, approximately 70%, was found from bottom-port effluent. Phosphorus concentrations under the higher flowrate and longer duration were statistically identical to those of the standard conditions study, indicating no effect from the higher hydraulic loading. The TKN removals suffered somewhat at the higher flow rate. Both concentrations in the small box and the upper ports in the large box were statistically higher than for the 4.1 cm/h flow.

In all but one case—the lower ports of the large box—nitrate production from the facilities was noted. A slight trend of nitrate concentrations decreasing with time generally was found, supporting a mechanism of washout of captured nitrate. Nitrate concentrations were up to 0.06 mg-N/L greater than input from the shallow ports and up to 0.16 mg-N/L greater from the lower ports. None of these concentrations, however, were statistically different from standard conditions. Effluent TN levels were higher than standard from both ports in the small box at the high flow and from the upper

Table 3.—Summary table for nutrients removal for boxes at high durations and flow rates.

	12-hour duration				Flowrate doubled (8.1 cm/hr)			
	P (mg/L)	TKN (mg/L)	NO ₃ -N (mg/L)	TN ^a (mg/L)	P (mg/L)	TKN (mg/L)	NO ₃ -N (mg/L)	TN ^a (mg/L)
Small Box								
Input	0.44 ± 0.02	3.2 ± 0.41	0.34 ± 0.01	3.5 ± 0.41	0.44 ± 0.00	3.5 ± 0.94	0.39 ± 0.07	3.9 ± 0.87
Average ± Std. Dev.								
U	0.39 ± 0.05	2.3 ± 0.65	0.40 ± 0.07	2.7 ± 0.59 ^d	0.36 ± 0.04	3.0 ± 0.68 ^d	0.40 ± 0.07	3.4 ± 0.63 ^d
L	0.14 ± 0.04	1.2 ± 0.48	0.50 ± 0.13	1.7 ± 0.43	0.13 ± 0.03	2.3 ± 0.27 ^d	0.43 ± 0.10	2.8 ± 0.24 ^d
Removal %								
U	11 ± 13	28 ± 20	(-15) ± 19	24 ± 16	18 ± 9	12 ± 18	(-2) ± 12	11 ± 15
L	69 ± 9	63 ± 14	(-45) ± 35	52 ± 11	70 ± 6	31 ± 13	(-8) ± 13	27 ± 13
Mass	81 ± 7,	77 ± 11,	10 ± 49,	70 ± 15,	79 ± 7,	52 ± 20,	26 ± 22,	49 ± 21,
Removal (%)	78 ± 8 ^c	74 ± 12 ^c	8 ± 48 ^c	67 ± 15 ^c	52 ± 11 ^c	32 ± 3 ^c	15 ± 8 ^c	30 ± 4 ^c
Large Box								
Input	—	—	—	—	0.50 ± 0.00	3.7 ± 0.28	0.33 ± 0.01	4.0 ± 0.29
Average ± Std. Dev.								
U	—	—	—	—	0.62 ± 0.10 ^b	2.7 ± 0.45 ^d	0.36 ± 0.03	3.1 ± 0.44
M	—	—	—	—	0.27 ± 0.09	2.2 ± 1.2	0.40 ± 0.01	2.6 ± 1.2
L	—	—	—	—	0.15 ± 0.12	1.1 ± 1.0	0.22 ± 0.12	1.4 ± 1.1
Removal %								
U	—	—	—	—	(-24) ± 19 ^b	26 ± 26	(-9) ± 8	23 ± 14
M	—	—	—	—	47 ± 18	42 ± 28	(-24) ± 1	37 ± 26
L	—	—	—	—	71 ± 24	70 ± 27	32 ± 36	67 ± 25
Mass	—	—	—	—	96 ± 5,	95 ± 5,	92 ± 6,	95 ± 5,
Removal (%)	—	—	—	—	73 ± 13 ^c	73 ± 14 ^c	70 ± 14 ^c	72 ± 14 ^c

(U=Upper Ports; M=Middle Ports; L=Lower Ports).

^a TN defined as TKN + NO₃-N.^b One point sequestered. Without this point, values are 1.1 ± 0.90 mg/L and (-113) ± 179%.^c Considers mass lost due to “bypass” in experiments where head exceeded ~15 cm. See text for details.^d t-test indicates significantly different from standard conditions at 95% confidence level.

ports for the long duration, again, primarily as a result of the reduced effectiveness noted for TKN.

High values of pollutant mass removals again reflect the attenuation of water in the boxes, although treatment efficiencies are somewhat lower as a result of the higher flow/duration. In these experiments, however, a second mass removal value is calculated, assuming that the flowrate was held at the original target value and that all pollutants lost to bypass are not removed, thus decreasing the overall mass removal efficiency. With the 12-h duration, the effect is slight because minimal bypass occurred. A greater effect resulting from the bypass is noted for the doubled input flowrate. For example, the mass removal decreased from the standard conditions value of 82 ± 10% to 79 ± 7% based on the mass of P that was added, but falls to 52 ± 11% considering that a fraction of the input flow was “bypassed” without treatment. Nonetheless, even considering this bypass, net mass reduction of nitrate was always found, even though concentrations were higher than input.

Runoff pH and Nutrient Concentration Effects. Some effects, mostly unfavorable, from varying the runoff pH were observed (Table 4). Desorption and release of P was noted at the upper ports for both higher and lower pH flows. Dissolved phosphorus speciation should be dominated by H₂PO₄⁻ and HPO₄²⁻ from pH 6 to 8. Studies with soils have suggested that HPO₄²⁻ is the active

adsorbing species (Barrow, 1983); experiments have shown that, generally, P sorption decreases slightly with pH under acidic conditions, but there is little dependence on pH in the neutral regime. Nonetheless, the pH effect did not manifest at the lower ports where the pH had a greater chance to buffer. No effect was noted for TKN. Effluent nitrate was significantly higher from lower ports at both pH values. These nitrate levels were also demonstrated by high TN levels. Neither TKN nor nitrate aqueous speciation should be affected by pH. Microbial denitrification rates should not vary greatly in this pH range (Rittmann and McCarty, 2001), and the authors are hesitant to draw major conclusions here. The results indicate a need for more work and may be artifacts of multiple N loadings because these experimental sets were some of the last performed. These results are also in contrast to those noted for the parallel studies with metals, in which variations in pH were buffered by the soil, producing little variation in removal efficiencies (Davis et al., 2003).

Input of higher nutrient concentrations to the small box always resulted in higher output concentrations (Table 5). This difference was statistically significant in every case, except for the lower port P. From a percent-removed perspective, however, the high concentration values are similar to those of the standard values. These results suggest that nutrient reduction through bioretention is best described by a constant removal ($1 - C/C_0$) or input/output ratio (C/C_0) and that high output concentrations will result from

Table 4.—Summary table for nutrients removal for boxes at different pH.

	pH 6				pH 8			
	P (mg/L)	TKN (mg/L)	NO ₃ -N (mg/L)	TN ^a (mg/L)	P (mg/L)	TKN (mg/L)	NO ₃ -N (mg/L)	TN ^a (mg/L)
Small Box								
Influent	0.47 ± 0.03	3.5 ± 0.12	0.32 ± 0.00	3.9 ± 0.12	0.47 ± 0.02	3.8 ^b	0.34 ± 0.00	4.1 ^b
Ave ± Std. Dev.								
U	0.48 ± 0.04 ^c	2.3 ± 0.34	0.49 ± 0.15	2.8 ± 0.20 ^c	0.50 ± 0.03	2.2 ± 0.01	0.55 ± 0.19	2.9 ± 0.18
L	0.14 ± 0.04	1.0 ± 0.28	0.82 ± 0.18 ^c	1.8 ± 0.35 ^c	0.12 ± 0.04	0.98 ± 0.05	0.94 ± 0.23 ^c	2.1 ± 0.22 ^c
Removal (%)								
U	(-1) ± 7	36 ± 10	(-52) ± 48	29 ± 6	(-6) ± 8	42 ± 0	(-60) ± 56	30 ± 4
L	72 ± 7	72 ± 7	(-153) ± 56	53 ± 8	74 ± 8	74 ± 1	(-175) ± 67	50 ± 5
Mass								
Removal (%)	86 ± 2	88 ± 7	(-6) ± 26	80 ± 9	92 ± 4	95	30 ± 18	91

U = Upper Ports; M=Middle Ports; L = Lower Ports.

^a TN defined as TKN + NO₃-N.

^b One data set sequestered.

^c t-test indicates significantly different from standard conditions at 95% confidence level.

more concentrated inputs. This concept, however, is less supported by the half-concentration data. In this case, with one exception, output concentrations are not significantly different from those of the standard conditions; correspondingly, percent removals are less.

This may be evidence of a threshold lower concentration that would be difficult to breach and that very low effluent nutrient concentrations may be difficult to obtain, which was also apparent in the metals removal data.

Table 5.—Summary table for nutrient removal for boxes at different nutrient concentrations.

	Double concentration				Half concentration			
	P (mg/L)	TKN (mg/L)	NO ₃ -N (mg/L)	TN ^a (mg/L)	P (mg/L)	TKN (mg/L)	NO ₃ -N (mg/L)	TN ^a (mg/L)
Small Box								
Influent	0.88 ± 0.13	5.5 ± 1.5	0.50 ± 0.02	6.0 ± 1.5	0.37 ± 0.20	1.4 ± 0.87	0.27 ± 0.01	1.6 ± 0.86
Ave ± Std. Dev.								
U	0.87 ± 0.32	4.4 ± 0.83	0.62 ± 0.13	5.0 ± 0.74	0.35 ± 0.08	0.24 ± 0.15 ^b	0.42 ± 0.06	0.66 ± 0.17 ^b
L	0.15 ± 0.08	1.6 ± 0.57	1.0 ± 0.46 ^b	2.6 ± 0.47	0.14 ± 0.06	0.62 ± 0.30	0.46 ± 0.04	1.1 ± 0.29
Removal (%)								
U	4 ± 25	17 ± 25	(-25) ± 29	14 ± 21	(-17) ± 27	82 ± 11	(-58) ± 18	59 ± 24
L	84 ± 7	69 ± 16	(-104) ± 97	55 ± 11	64 ± 12	31 ± 51	(-73) ± 18	14 ± 48
Mass								
Removal (%)	91 ± 8	83 ± 17	31 ± 11	79 ± 18	81 ± 1	66 ± 36	15 ± 13	58 ± 37
Large Box								
Influent ^d	—	—	—	—	0.28	2.1	0.24	2.4
Ave ± Std. Dev.								
U	—	—	—	—	0.51 ± 0.07	0.15 ± 0.07	0.24 ± 0.01	0.75 ± 0.06
M ^d	—	—	—	—	0.23	1.3	0.33	1.6
L	—	—	—	—	0.09 ± 0.02	1.1 ± 0.07	0.15 ± 0.08	1.2 ± 0.0
Removal (%)								
U	—	—	—	—	(-80) ± 25	76 ± 3	0 ± 4	69 ± 3
M ^d	—	—	—	—	17	38	(-35)	31
L	—	—	—	—	69 ± 8	50 ± 3	40 ± 31	49 ± 0
Mass								
Removal (%)	—	—	—	—	92	94	96	94

U = Upper Ports; M=Middle Ports; L = Lower Ports.

^a TN defined as TKN + NO₃-N.

^b t-test indicates significantly different from standard conditions at 95% confidence level.

^c One data set sequestered.

^d Only one sample for nutrients analysis.

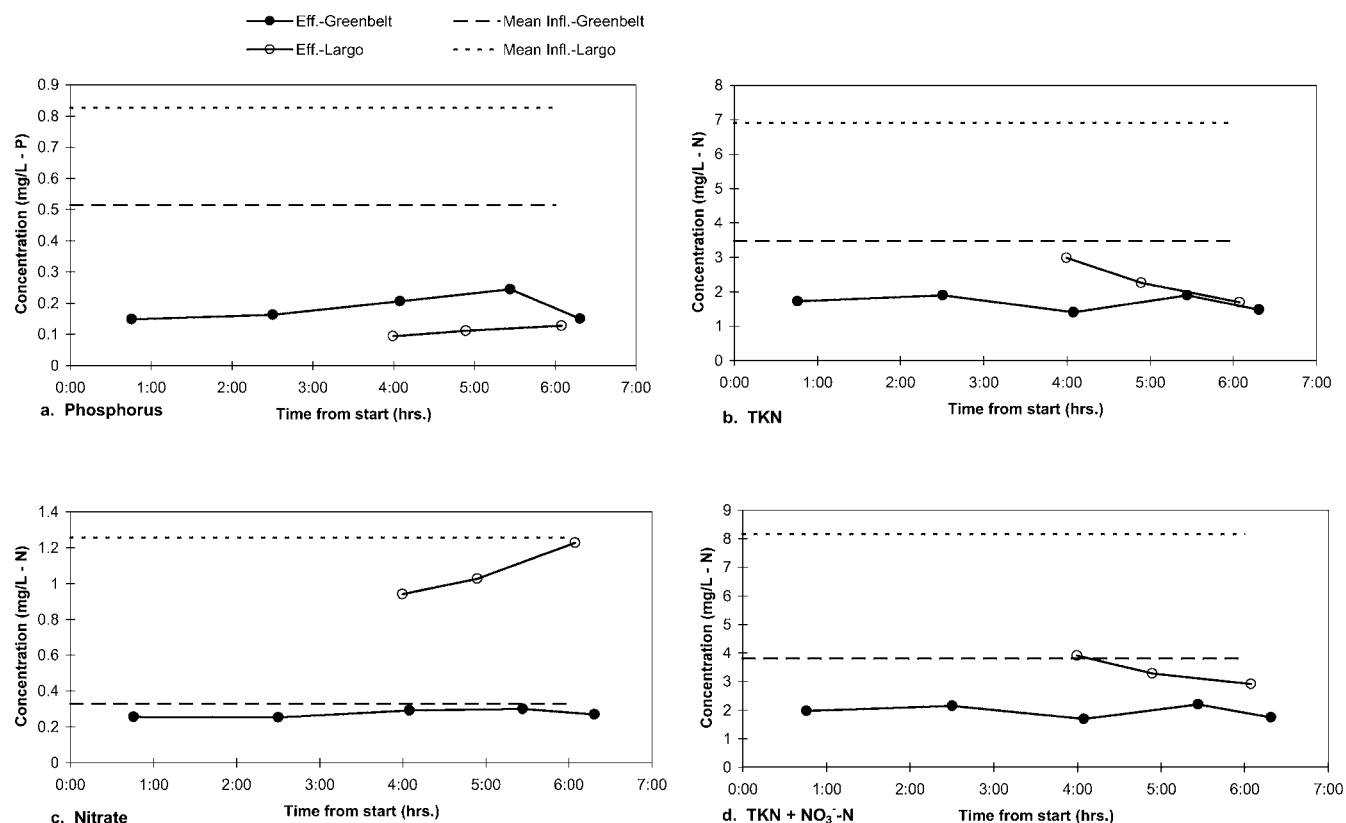


Figure 1—Field bioretention performance during synthetic runoff application: (a) phosphorus, (b) TKN, (c) nitrate, and (d) total N = TKN + NO₃.

Again, both the variable pH and nutrient concentration mass removal data demonstrate the importance of volume attenuation. Mass removals are always greater than concentration-based removals, and, in four of the five cases, positive nitrate mass removal was found, even though effluent concentrations were almost always higher than input.

Field Study Results. Reductions of nutrients concentrations were observed in both field investigations. Sampling results are presented in Figures 1a through d. The effluent concentrations were generally constant over the sampling time period. The total phosphorous removal at Greenbelt was good, at $65 \pm 8\%$, and that at Largo was $87 \pm 2\%$, which is excellent removal, with effluent concentrations just above 0.1 mg/L P (Figure 1a). Good-to-excellent removal agrees with data found in the box studies. Treatment efficiency for TKN was $52 \pm 7\%$ at Greenbelt and $67 \pm 9\%$ at Largo, which is good removal that demonstrates very good agreement with laboratory results. The removal for nitrate was poor, at only $16 \pm 6\%$ and $15 \pm 12\%$, respectively, for Greenbelt and Largo, which, based on the box data, was not unexpected. The TN removal was $49 \pm 6\%$ and $59 \pm 6\%$.

Comparing these systems to each other and the boxes, the soil media at Greenbelt contained less sand, but was deeper (it was based on an older design). The vegetation at Greenbelt is thick, and the soil structure should be well-developed after 10 years of operation. The Largo facility is an engineered soil matrix with more sand that was only two years old when this study was completed. It is also shallower than the Greenbelt facility. Based on these differences, the Greenbelt facility would be expected to provide

better nutrient treatment, but this was not found. Overall, nutrient removal efficiencies found in the two field facilities proved very similar to each other and to those demonstrated in the box studies and should lend credence to the field applicability of conclusions developed with the boxes.

Bioretention Depth Effects. Combining removal data from the box studies at standard conditions at the respective depths with the field results allow a cursory examination of the effect of facility depth on nutrient removal (Figure 2). The scatter of the nutrients data is much greater than that found in a similar exercise for metals (Davis et al., 2003), but relatively good agreement is still noted between the laboratory and field studies, even though the media are not identical. Phosphorus removals increased up to approximately 60- to 80-cm depth (Figure 2a), plateauing at 70 to 85% found in the field studies. Most soils have a significant capacity to adsorb phosphorus at neutral pH, and adsorption onto silt and clay minerals was likely the dominant phosphorus uptake mechanism.

In contrast to the phosphorus, most of the TKN removal occurred within the top few centimeters (Figure 2b). Beyond this, the removal was fairly constant, averaging approximately 55 to 65%. The significant removal occurring within the first few centimeters suggests that the surface mulch may be responsible for this treatment. The removal of organic N via sorption processes should be enhanced by the organic mulch layer. The depth trends for P and TKN are somewhat similar to those found for copper, lead, and zinc (Davis et al., 2003). With the metals, nearly complete removal was always noted by the shallowest ports. With P and TKN, however, the plateauing is more gradual, and facility depth becomes more

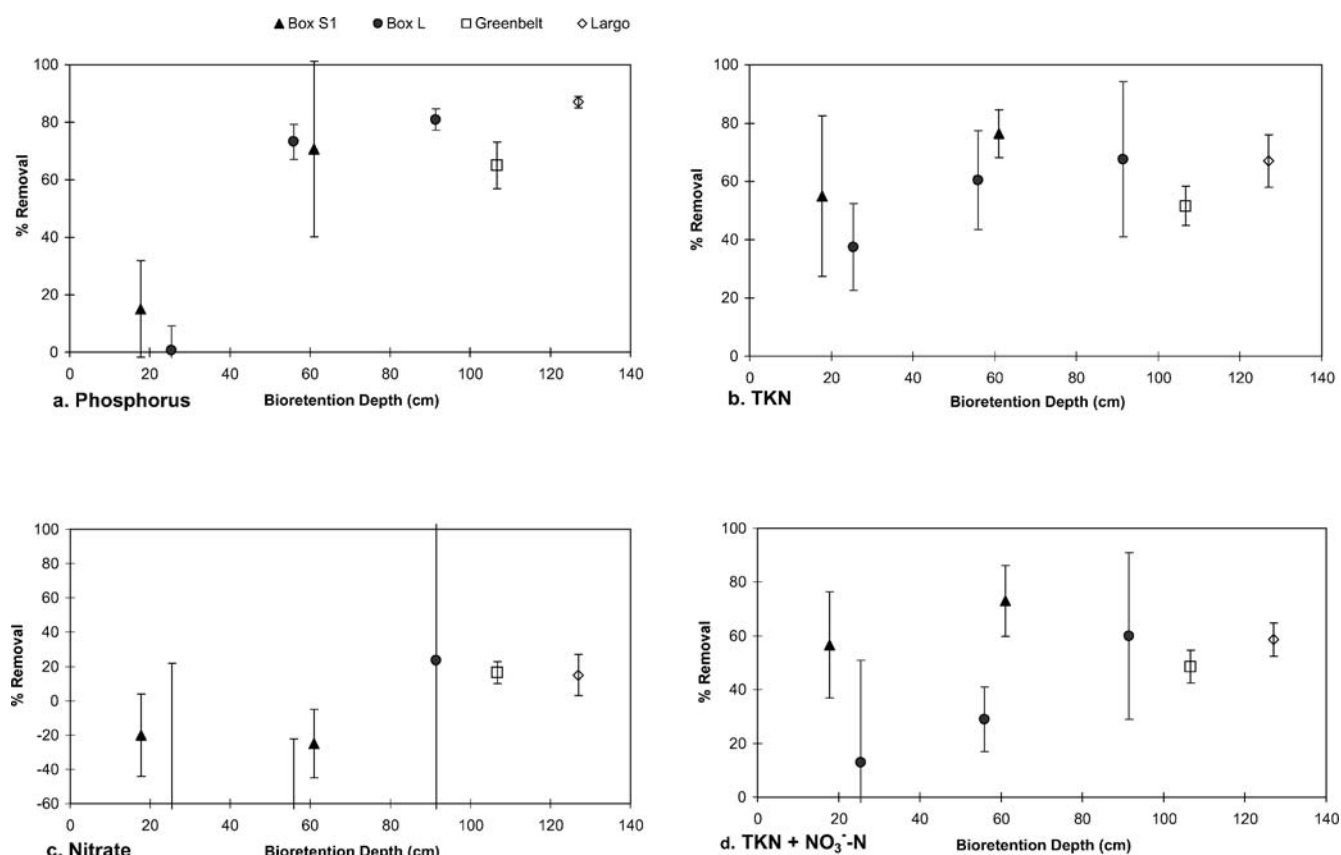


Figure 2—Pollutant removals as a function of bioretention depth (data for boxes from Davis et al. [2001]): (a) phosphorus, (b) TKN, (c) nitrate, and (d) total N = TKN + $\text{NO}_3\text{-N}$.

important. The similarity in the shapes of these curves suggests that the mechanism of removal, which is probably some type of moderately strong adsorption process, is similar for both.

Although nitrate removal results were erratic in the laboratory experimentation, the field results were more consistent, demonstrating 15 to 20% removal. Nitrate is very mobile through a soil column, and minimal uptake was expected. Shallow sampling ports in the laboratory boxes consistently showed nitrate levels higher than the input, suggesting conversion of captured organic nitrogen to nitrate (two of these points are below the lower axis on Figure 2c). Nonetheless, release of transformed antecedent nitrogen was not indicated in the two field studies. Nitrate does not sorb to any significant degree onto soils, so bioretention facilities are not expected to provide any nitrate removal; consequently, any reduction is considered as a bonus. Depending on the flow and redox characteristics of the bioretention media, some limited denitrification may be occurring. A few recent studies have begun to investigate this process in bioretention (Hunt et al., 2002; Kim et al., 2003), and more work is warranted.

The TN data are dominated by TKN. Approximately 50 to 80% removal was found at the greatest depths, which is in agreement with TN results from bioretention columns reported by Hunt et al. (2002). Regardless of the scatter, all data indicate some degree of total nitrogen reduction through bioretention treatment, providing benefits for potential water quality improvements with respect to this critical nutrient.

The role of vegetation is difficult to assess in a short-term experiment. The authors hypothesize that the plants play a very

small role in the direct uptake and attenuation of the pollutants during the actual rainfall event. The infiltration process is too rapid and would be dominated by physical and chemical mechanisms in the mulch and soil matrix. Nonetheless, the vegetation (and macroinvertebrates) would play a greater role in determining the long-term structure and makeup of the soil. Additionally, plant uptake should be important for long-term pollutant uptake and management.

Environmental Significance: Nutrients and Bioretention. Different pathways dominate when comparing the long-term fates of phosphorus and nitrogen compounds. Although P is biologically active, no significant ecological transport pathway exists in which it can be converted to gaseous form, as with nitrogen. Thus, a bioretention fate analysis with P is similar to that with metals; P will accumulate in the facility with an opportunity for its removal via vegetative uptake and harvesting or provisions must be made for long-term sequestration in the soil media. A cumulative P loading can be estimated via assuming a treated runoff volume, which is calculated by assuming a 90-cm per year rainfall, 90% to runoff ($c = 0.9$) and a 30:1 concentration of drainage area to BMP area. The result is 24 300 L runoff/ m^2 of BMP/y. Using a runoff P concentration of 0.35 mg/L and a reasonable bioretention capture efficiency of 75% (Figure 2a), an annual value of accumulated P is calculated as 6.4 g-P/ m^2 /y. Assuming a media bulk density of 1600 kg/ m^3 and a media depth of 0.75 m, this requires a P uptake capacity of 5.3 mg P/kg media/y, which is not unreasonable considering that soil P adsorption capacities range up to several hundred milligrams per kilogram (Singh and Uehara, 1999). System modification could include the incorporation of

aluminum or iron oxide materials (Codling et al., 2000) to the bioretention media to enhance the P uptake capacity. These materials provide an excess of adsorption sites for P and can precipitate and/or co-precipitate P compounds.

Evaluation of nitrogen fate is more complex. First considering nitrate, minimal adsorption or physicochemical interaction with the soil media is expected. The slight reduction in nitrate levels found in the field and a few of the box studies can be attributed to limited denitrification that occurs in the soil column. Active microbial populations are expected to be supported by vegetation in the field facilities. Low levels of denitrification may be occurring in isolated microcosms of the soil media where anoxic conditions prevail.

Organic nitrogen should be sorbed by organic matter in the soil and, specifically, in the mulch layer. These organic-rich bioretention layers should also support significant microbial populations, which should be readily able to degrade captured organic N. Aerobic metabolism of organic N should result in the production of ammonium and, eventually, nitrate through ammonification and nitrification (Kadlec and Knight, 1996). These microbial processes are expected to be continuously ongoing throughout the resting period between runoff events. Such conversion of previously captured organic N to nitrate (which is subsequently washed out) can partially negate the efficient organic-N removal mechanisms inherent to bioretention.

If properly designed and managed, the vegetation may play a significant role in the bioretention nutrient mass balance. An uptake of 51 g-N/m²/y can be estimated from information on typical wetland plants (Kadlec and Knight, 1996). The yearly TN loading (at 4 mg-N/L organic N and 0.4 mg-N/L nitrate) to bioretention, based on the assumptions detailed above, is estimated at 107 g-N/m²/y. Of this value, with current design, approximately one-half is captured, giving an accumulation of 54 g-N/m²/y. Therefore, plant assimilation could possibly remove greater than 90% of captured nitrogen, demonstrating an important role for vegetation in the bioretention nitrogen cycle. Additionally, plant matter is approximately 0.25% P; thus, using the same uptake information, an assimilation rate of approximately 18 g-P/m²/y is estimated. This value exceeds the P input rate calculated above, suggesting that plant harvesting may also be a viable option for the removal of captured P from a bioretention facility. Using plant species with high nutrient uptake rates (e.g., Sharma et al., 2004) may provide these benefits for sustainable bioretention operation.

Of course, most of this nutrient uptake will occur in the spring and early summer, when vegetative growth is maximum. This vegetation must be cut and removed from the facility to complete the nutrient mass removal process. Vegetation that is left to decay will release any nutrients that were originally assimilated. Thus, a thick vegetative growth may be beneficial to bioretention nutrient management. Accordingly, periodic cutting and removal of plant material and mulch as routine maintenance should be considered for the elimination of accumulated nutrients in bioretention facilities. The vegetation should then enter into a composting process for further management of the biomass and associated nutrients.

Summary and Recommendations

Bioretention has been demonstrated to be promisingly efficient in the removal of phosphorus and organic nitrogen from infiltrating runoff. Experiments showed that bioretention facilities of 60 to 80 cm depth yielded 70 to 85% removal of phosphorus and 55 to 65% removal of TKN. These results were obtained with a sandy loam soil in several box studies and with two field facilities with different

designs; additional research should be undertaken to confirm these removal rates with other bioretention designs. These values agree with previous reports of total phosphorus removal via stormwater infiltration facilities (CWP, 2004; U.S. EPA, 1999), but are greater than the 39% TP reduction reported for Austin sand filters (Barrett, 2003).

These nutrients may be the target pollutants in residential and recreational areas where fertilizers may be washing off of managed lawn areas. Bioretention is minimally effective for nitrate removal (<20%), and biotransformation of some captured organic nitrogen to nitrate is indicated. The importance of promoting water infiltration from bioretention into surrounding soils should not be underestimated. Water that does not exit the bioretention facility to a surface water conduit will not transport the associated pollutant loadings. Water that infiltrates beyond the boundaries of the bioretention cell will be subjected to increased soil contact and longer reaction time for the reduction of nutrient loads. Evaporation and transpiration provide an additional demineralization route for the water, leaving behind and trapping pollutants.

Managing the growth and harvesting of vegetation in bioretention facilities has potential for removing a major portion of captured N and P. Modification of standard bioretention design to include the incorporation of an anoxic cell to promote denitrification could provide additional removal of input N (Kim et al., 2003), with a specific focus on nitrate, which is the most difficult form of N to address.

Of course, reductions in input nutrient levels through pollution prevention and educational measures will always provide benefits and should increase the efficiency of all runoff nutrient management technologies.

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